On the Symmetry of Low-Field Ordered Phase of $PrFe_4P_{12}$: ^{31}P NMR

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We have performed ^{31}P nuclear magnetic resonance (NMR) experiments on the filled skutterudite compound $PrFe_4P_{12}$ to investigate the exotic ordered phase at low temperatures and low magnetic fields. Analysis of the NMR line splitting in the ordered phase indicates that totally symmetric (Γ_1-type) staggered magnetic multipoles are induced by magnetic fields. This is incompatible with any type of quadrupole order at zero field. We conclude that the ordered phase has broken translational symmetry with the wave vector $\mathbf{Q} = (1, 0, 0)$ but the T_h point symmetry at the Pr sites is not broken by the non-magnetic Γ_1-type order parameter.

KEYWORDS: $PrFe_4P_{12}$, NMR, skutterudite, multipole moment, order parameter, hyperfine interaction

Intermetallic compounds with the filled-skutterudite structure RT_4X_{12} (R = rare earth, T = transition metal, X = pnictogen) has attracted strong recent attention because of a variety of intriguing phenomena in a common crystal structure such as metal-insulator transition,[1)] multipole ordering,[2)] exotic superconductivity,[3)] and anomalous phonons.[4)] Among them, $PrFe_4P_{12}$ shows a peculiar phase transition at T_A=6.5 K.[5)] The low temperature phase has no spontaneous magnetic moment at zero field[6)] and is suppressed by a magnetic field of 4–7 T dependent on the field directions,[5)] resulting in a heavy-fermion state with a large cyclotron effective mass $m_c^* = 81\, m_0$.[7)] The low temperature phase has a structural modulation with the wave vector $\mathbf{Q} = (1, 0, 0)$, indicating loss of $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ translation.[8)] Spatial ordering of distinct electronic states of two Pr^{3+} ions in the bcc unit cell was also observed by resonant X-ray scattering,[9)] and the field-induced staggered magnetization was observed by neutron scattering.[10)] Although these experiments and the elastic measurements[11)] suggest an antiferro-quadrupole order likely to be of Γ_{23}-type, direct identification of the order parameter has not been made yet.

In this letter, we report results of nuclear magnetic resonance (NMR) experiments on ^{31}P nuclei (spin 1/2) in a single crystal of $PrFe_4P_{12}$, focusing on the ordered phase. We observed field-induced splitting of the ^{31}P NMR lines below T_A. The results for various field directions revealed that the splitting is due to totally-symmetric staggered magnetic multipoles (octupole as well as dipole) belonging to the Γ_1 representation. We conclude that the order parameter at zero field has Γ_1 symmetry, excluding any type of quadrupole order.

In the filled skutterudite structure (the space group $Im\bar{3}$, T_h^5), Pr atoms are surrounded by an icosahedral cage of P atoms and form a body-centered cubic lattice as shown in Fig. 1.[6,12)] Iron atoms sit at the middle between the corner and the body-centered Pr atoms. Although all the P sites are crystallographically equivalent, they have different NMR frequencies in magnetic field because of anisotropic hyperfine interaction. For later discussion, we define six types of P sites giving distinct NMR frequencies for general field directions as P1$(0, u, v)$, P2$(0, \bar{u}, v)$, P3$(v, 0, u)$, P4$(v, 0, \bar{u})$, P5$(u, v, 0)$ and P6$(\bar{u}, v, 0)$, where u and v are the asymmetry parameters (Fig. 1).[13)]

If the direction of the external field $\mathbf{H}$ is invariant under a symmetry operation which transforms one P site to another, those two P sites must have the same NMR frequency. For example, P1, P3 and P5 sites (P2, P4, and P6 sites) transform each other by 120° rotation around [111], therefore, they should give a single NMR line for $\mathbf{H} \parallel [111]$. Likewise, for $\mathbf{H} \parallel [001]$, there should be three lines generated by three pairs of sites, (P1, P2), (P3, P4), and (P5, P6). For $\mathbf{H} \parallel [110]$, P5 and P6 become inequivalent and we expect four lines. Figure 2(a) shows the NMR spectra at T=50 K above T_A. We observed three, four, and two lines for $\mathbf{H}$ parallel to the [001], [110], and [111] directions, respectively. This agrees with the consequence of crystal symmetry. Detailed angle dependence of the resonance frequencies (not shown) leads to the site

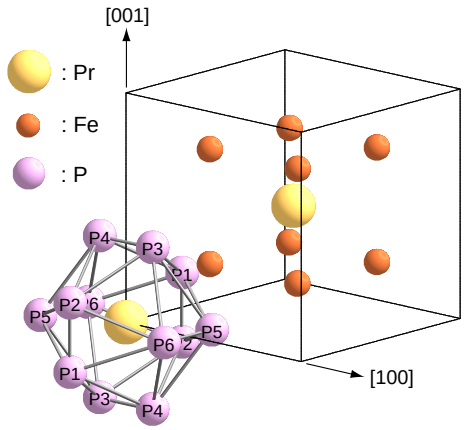

Fig. 1. (Color online) Schematic view of the crystal structure of $PrFe_4P_{12}$. The cage surrounding the body-centered Pr atom is omitted for clarity.

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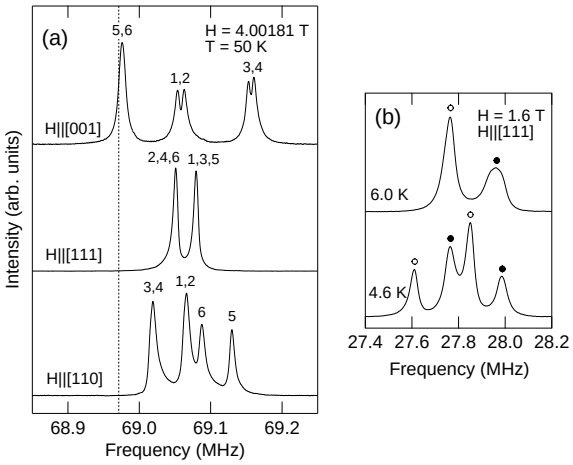

Fig. 2. (a) ^{31}P NMR spectra at 50 K obtained by Fourier transforming the spin-echo signals. The numbers indicate the P sites (P1–P6) to which each peak is assigned. The dotted line shows the reference frequency at zero shift. (b) ^{31}P NMR spectra at 6.0 K (above T_A) and at 4.6 K (below T_A) for the field of 1.6 T along [111]. NMR lines from P1, P3 and P5 sites (P2, P4 and P6 sites) are indicated by solid (open) circles.

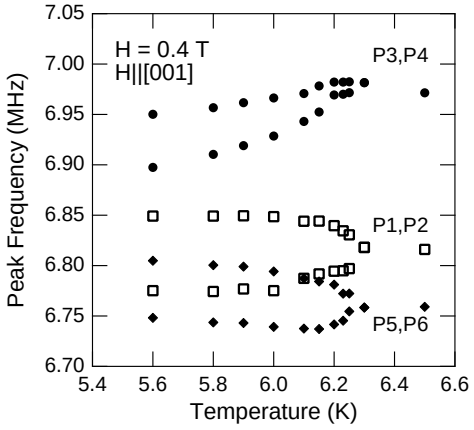

Fig. 3. Temperature dependence of the NMR frequencies near T_A=6.27 K for the field of 0.4 T along [001].

assignment shown in Fig. 2(a). The small splitting of the two high frequency lines for **H** ∥ [001] is probably due to nuclear spin-spin coupling.

On crossing T_A from above, each line splits into a pair of lines as shown in Figs. 2(b) and 3. The splitting grows continuously near T_A at low fields (0.4 T) as shown in Fig. 3. At higher fields above about 1.5 T, however, the splitting develops discontinuously and there is a narrow temperature range in the vicinity of T_A where the spectrum has both split and unsplit lines. This indicates that the second order phase transition at low fields changes to first order at higher fields, consistent with the results of specific-heat measurements.[5)]

We define the splitting of the hyperfine field ΔH as the frequency interval of the splitting divided by the nuclear gyromagnetic ratio γ_N. The field dependence of ΔH is plotted in Fig. 4 for various field directions at T=2 K.

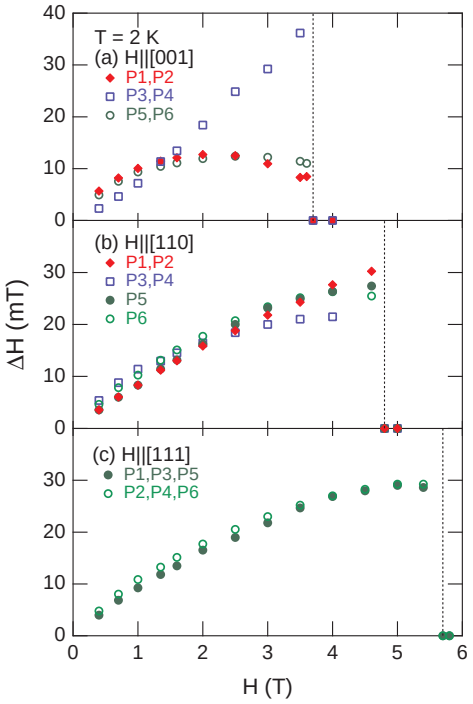

Fig. 4. (Color online) Field dependence of the splitting of the hyperfine field at 2 K for the field along (a) [001], (b) [110], and (c) [111]. The boundary between the ordered and uniform phases are shown by the dotted lines.

A remarkable result is that ΔH extrapolates to zero at H=0. Such a feature has been also observed in polycrystals by Ishida *et al.*[14)] The field dependences of ΔH are different for different sites. This is most evident for **H** ∥ [001], where ΔH for P3 and P4 increases monotonically with increasing field while ΔH for other sites shows a maximum. The field variation of ΔH is smooth in all cases without any jump or kink, indicating absence of additional phase transitions up to the boundary to the high-field heavy fermion (HF) state. A first-order

Table I. Symmetries of multipoles up to hexadecapoles in the T_h crystal field. The + and − signs show the parity under time reversal. The multipoles are defined in terms of the dipole **J** as follows.[16,17)] Quadrupoles: $O_2^0 = \frac{1}{2}(3J_z^2 - \mathbf{J}^2)$, $O_2^2 = \frac{\sqrt{3}}{2}(J_x^2 - J_y^2)$, $O_{\xi\eta} = \frac{\sqrt{3}}{2}\overline{J_\xi J_\eta}$, Octupoles: $T_{xyz} = \frac{\sqrt{15}}{6}\overline{J_x J_y J_z}$, $T_\xi^\alpha = \frac{1}{2}(2J_\xi^3 - \overline{J_\xi J_\eta^2} - \overline{J_\zeta^2 J_\xi})$, $T_\xi^\beta = \frac{\sqrt{15}}{6}(\overline{J_\xi J_\eta^2} - \overline{J_\zeta^2 J_\xi})$, Hexadecapoles: $H^0 = \sqrt{\frac{175}{48}}(J_x^4 + J_y^4 + J_z^4 - \frac{3}{5}\mathbf{J}^2(\mathbf{J}^2 - \frac{1}{3}))$, $H_\xi^\alpha = \frac{\sqrt{35}}{8}(\overline{J_\eta^3 J_\zeta} - \overline{J_\eta J_\zeta^3})$, $H_\xi^\beta = \frac{\sqrt{5}}{8}(2\overline{J_\xi J_\eta^2 J_\zeta} - \overline{J_\eta^3 J_\zeta} - \overline{J_\eta J_\zeta^3})$. Here ξ, η, ζ represent x, y, z and their cyclic permutation. The bars on products denote summation over all permutations of thier subscripts. Since $(T_x^\alpha, T_y^\alpha, T_z^\alpha)$ and $(T_x^\beta, T_y^\beta, T_z^\beta)$ $((H_x^\alpha, H_y^\alpha, H_z^\alpha)$ and $(H_x^\beta, H_y^\beta, H_z^\beta))$ have the same symmetry Γ_4^- (Γ_4^+) in the T_h group, they can be mixed.

Symmetry	Magnetic multipoles	Nonmagnetic multipoles
$T_h(\Gamma_1^+)$	—	H^0
$T_h(\Gamma_{23}^+)$	—	O_2^0, O_2^2, H_u, H_v
$T_h(\Gamma_4^+)$	—	$O_{xy}, O_{yz}, O_{zx}, H_x, H_y, H_z$
$T_h(\Gamma_1^-)$	T_{xyz}	—
$T_h(\Gamma_4^-)$	$J_x, J_y, J_z, T_x, T_y, T_z$	—

Table II. Symmetries of multipoles in the T_h crystal field in magnetic fields. The numbers in parentheses in the fifth column indicate the equivalent P sites and the last column shows the number of NMR lines for a single P_{12} cage in the presence of the magnetic multipoles. They should be multiplied by two to get the total number of lines in the antiferro-multipole ordered phase with $\mathbf{Q} = (1, 0, 0)$.

Field directions	Symmetry	Magnetic multipoles	Nonmagnetic multipoles	Equivalent sites	Number of lines
[001]	$C_{2v}(\Gamma_1)$	J_z, T_z	$O_2^0, O_2^2, H^0, H_u, H_v$	(1,2), (3,4), (5,6)	3
	$C_{2v}(\Gamma_2)$	T_{xyz}	O_{xy}, H_z	(1,2), (3,4)	4
	$C_{2v}(\Gamma_3)$	J_x, T_x	O_{zx}, H_y	(1,2), (5,6)	4
	$C_{2v}(\Gamma_4)$	J_y, T_y	O_{yz}, H_x	(3,4), (5,6)	4
[110]	$C_{1h}(\Gamma_1)$	$J_x, J_y, T_x, T_y, T_{xyz}$	$O_2^0, O_2^2, O_{xy}, H^0, H_u, H_v, H_z$	(1,2), (3,4)	4
	$C_{1h}(\Gamma_2)$	J_z, T_z	O_{yz}, O_{zx}, H_x, H_y	—	6
[111]†	$C_3(\Gamma_1)$	J_c, T_c, T_{xyz}	O_c, H^0, H_c	(1,3,5), (2,4,6)	2
	$C_3(\Gamma_{23})$	$(J_a, J_b), (T_a, T_b)$	$(O_2^0, O_2^2), (O_a, O_b), (H_u, H_v), (H_a, H_b)$	—	6

†a-, b- and c-components of the multipole Ψ ($= J, O, T, H$) are defined as $\Psi_a = \frac{1}{\sqrt{6}}(-\Psi_x - \Psi_y + 2\Psi_z)$, $\Psi_b = \frac{1}{\sqrt{2}}(\Psi_x - \Psi_y)$, and $\Psi_c = \frac{1}{\sqrt{3}}(\Psi_x + \Psi_y + \Psi_z)$, respectively, where (Ψ_x, Ψ_y, Ψ_z) is either (J_x, J_y, J_z), (O_{yz}, O_{zx}, O_{xy}), (T_x, T_y, T_z) or (H_x, H_y, H_z).

transition to the HF phase is apparent from the sudden vanishing of ΔH at the phase boundary.

Detailed examination of angle dependence of the spectra below T_A reported in ref. 15 revealed that all of the NMR lines above T_A split always into two lines and ΔH never vanishes for any field direction. Obviously, the doubling of the NMR lines should be ascribed to the loss of $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ translation and the distinct electronic states of the two Pr ions at the corner (PrI) and the body center (PrII) of the original bcc lattice.[8,9] This should divide each of the P1–P6 sites into two sublattices P1(I)–P6(I) and P1(II)–P6(II). The former (latter) belongs to the P_{12} cage surrounding the PrI (PrII) sites. We should stress that there is no additional line splitting, i.e., the number of NMR lines from each of these cages is exactly the same as the number of lines above T_A. This means that the T_h point symmetry at both Pr sites is preserved below T_A, which is not compatible with any type of quadrupole ordering. In the following, we provide more precise arguments on these points.

The hyperfine field at P nuclei is determined by the spin density distribution of Pr-4f electrons through the dipolar and the transferred hyperfine interactions. The very local nature of the latter interaction causes nuclei to couple not only to dipole moments but to octupoles and higher order magnetic multipoles. This is because the local spin density near a P nucleus can be nonzero when a Pr ion has finite expectation value of a high order magnetic multipole, even if the dipole moment, or the spatial integration of the spin density, is zero. Such a possibility has been first recognized by Sakai *et al.*[18] in their analysis of the NMR data on CeB_6.[19]

Magnetic and nonmagnetic multipoles up to hexadecapoles are presented in Table I as the basis of irreducible representations of the T_h group. In magnetic fields, they are decomposed into sets of smaller number of basis for reduced symmetries as shown in Table II. The NMR line splitting ΔH is due to some staggered magnetic multipoles with $\mathbf{Q} = (1, 0, 0)$. The vanishing ΔH at zero field indicates that these staggered multipoles also disappear at zero field. Therefore, the order parameter (OP) at zero field must be a nonmagnetic staggered multipole, which is even with respect to the time reversal and does not couple to nuclear magnetic moments. As discussed by Shiina *et al.*,[16] however, OP at zero field and the field-induced multipoles must belong to the same irreducible representation of the symmetry group reduced by the magnetic field. Thus identification of the field-induced magnetic multipoles allows us to determine the symmetry of OP at zero field.

Using the invariant form of the hyperfine coupling at the P sites in the filled skutterrudite structure,[15,20] the difference of the hyperfine fields at Pn(I) and Pn(II) (n=1–6), $\Delta\mathbf{H}(n) = (\Delta H_x^{(n)}, \Delta H_y^{(n)}, \Delta H_z^{(n)})$, is given for n=1 and 2 as

$$\begin{aligned}&(\pm c_{11}T^s_{xyz} + c_{12}J^s_x + c_{13}T^s_x,\\ &c_{21}J^s_y + c_{23}T^s_y \pm (c_{22}J^s_z + c_{24}T^s_z),\\ &\pm (c_{32}J^s_y + c_{33}T^s_y) + c_{32}J^s_z + c_{34}T^s_z),\end{aligned} \tag{1}$$

where T^s_{xyz}, T^s_ξ, and J^s_ξ are the staggered octupole and dipole moments and c_{ij} is the hyperfine coupling constants. For terms with $\pm$, the + (−) sign should be taken for P1 (P2). Expressions for P3 and P4 (P5 and P6) are obtained by applying once (twice) simultaneous cyclic permutations $x \to y \to z \to x$ in the subscripts of the multipoles and $\Delta H_x \to \Delta H_y \to \Delta H_z \to \Delta H_x$. Since the external field is much larger than the hyperfine field, ΔH is equal to $\Delta\mathbf{H} \cdot \mathbf{h}$, where $\mathbf{h}$ is the unit vector along the field direction. From eq. (1), we can determine the equivalent sites and the number of NMR lines in the presence of these field-induced magnetic multipoles as shown in the last two columns of Table II. For example, if a staggered component of J_y or T_y were induced by the field along [001], eq. (1) tells $\Delta H_z^{(1)} \neq \Delta H_z^{(2)}$. Thus P1 and

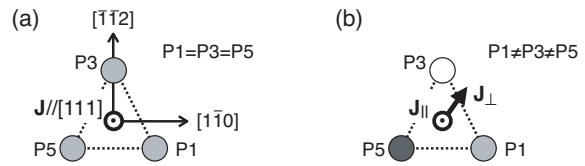

Fig. 5. Field-induced dipole $\mathbf{J}$ for $\mathbf{H} \parallel [111]$. (a) When $\mathbf{J}$ is parallel to $\mathbf{H}$. i.e. $J_c \neq 0$ and $(J_a, J_b) = 0$ in the notation of Table II, P1, P3 and P5 are all equivalent. (b) If J_a or $J_b \neq 0$, P1, P3 and P5 become inequivalent due to loss of three-fold rotational symmetry about [111].

Table III. Reduction of irreducible representations of the T_h group in magnetic fields.

zero field	$\mathbf{H} \parallel [001]$	$\mathbf{H} \parallel [110]$	$\mathbf{H} \parallel [111]$
T_h	C_{2v}	C_{1h}	C_3
$\Gamma_1^{\pm}$	Γ_1	Γ_1	Γ_1
$\Gamma_{23}^{\pm}$	$2\Gamma_1$	$2\Gamma_1$	Γ_{23}
$\Gamma_4^{\pm}$	$\Gamma_2+\Gamma_3+\Gamma_4$	$\Gamma_1+2\Gamma_2$	$\Gamma_1+\Gamma_{23}$

P2 should give distinct NMR lines and there should be four lines from a single cage.

As mentioned before, the number of NMR lines for a single P_{12} cage remains unchanged upon entering into the ordered phase: three, four and two for $\mathbf{H} \parallel [001]$, [110] and [111], respectively. From Table II, we can conclude that the field-induced magnetic multipoles must have the Γ_1 symmetry for all field directions. In other words, only the totally-symmetric multipoles can avoid additional line splitting. For dipoles, this means that the induced dipole moment is always parallel to the external field, which is consistent with the neutron scattering measurements.[10] This can be intuitively understood as illustrated in Fig. 5 for the case $\mathbf{H} \parallel [111]$.

Thus the OP must be totally symmetric in magnetic fields. Inspecting Table II, we find there is no such quadrupole. For example, Γ_4-type quadrupoles O_{xy}, O_{yz} and O_{zx} induce magnetic multipoles which do not belong to Γ_1 for $\mathbf{H} \parallel [001]$. Quadrupoles O_2^0 and O_2^2 of Γ_{23} type induce dipole moments perpendicular to the field for $\mathbf{H} \parallel [111]$. Both cases lead to more NMR lines than experimentally observed. Therefore, there should not be antiferro-quadrupole order at zero field.

One notices at this point that the OP at zero field should be also totally symmetric. We can see this formally by studying reduction of irreducible representations of the T_h group under the [001], [110] and [111] fields as shown in Table III. It is apparent that only the Γ_1 representation at zero field has always a Γ_1 component in magnetic fields irrespective of the field direction.

At present, we cannot identify the detailed form of the OP because the number of NMR lines depends only on the symmetry of the OP in magnetic fields. The OP may thus include various multipoles of different ranks in general, as far as they are nonmagnetic and have the Γ_1 symmetry. Such a multipole order can be caused, for example, by alternate breathing of the icosahedral cages which preserves local T_h symmetry at the Pr sites. This type of lattice distortion has been observed in the insulating phase of $PrRu_4P_{12}$,[21] where the antiferro order of the hexadecapole $H^0 \propto J_x^4+J_y^4+J_z^4$ has been proposed.[22] In fact, this is the only totally-symmetric nonmagnetic multipole among those listed in Table I. Quantitative analyses of the splitting ΔH as a function of direction and magnitude of the field will give further information about the OP such as the rank of a dominant multipole. Some phenomenological approaches are in progress,[15,20] although a microscopic theory is needed to uncover the mechanism of this interesting phase transition.

In conclusion, we have presented ^{31}P NMR data in a single crystal of $PrFe_4P_{12}$, confirming antiferro order of nonmagnetic multipoles at low fields. There exist field-induced staggered magnetic multipoles, which is compatible only with the totally-symmetric order parameter at zero field. The T_h point symmetry at the Pr sites is thus preserved in the ordered phase, excluding any type of quadrupole order.

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